

## SECTION 5.0 TREATABILITY TESTING

Following site characterization and identification of prospective reactive media candidates, bench-scale treatability testing is conducted to aid the design. Treatability testing serves the following purposes:

- Screening and selecting a suitable medium (e.g., iron) for the reactive cell
- Estimating the half-life of the degradation reaction and determining flowthrough thickness of the reactive cell
- Evaluating the longevity of the wall.

Treatability tests can be conducted in a batch or column (continuous) mode. Most researchers now agree that batch tests are useful mainly as an initial screening tool for evaluating different media or for assessing the degradability of contaminants hitherto known to be recalcitrant (Sivavec, 1996; ETI, 1996). For most other purposes, researchers favor column tests for the following reasons:

- Design parameters are determined under dynamic flow conditions. As concentrations of contaminants and inorganic change with the distance traveled through the reactive cell, they can be measured by installing a number of intermediate sampling ports along the length of the column.
- Half-lives measured through column tests are generally more reliable than half-lives measured through batch tests.
- Nonlinear sorption to nonreactive sorption sites (Burris et al., 1995) is better simulated in columns.
- Reaction products may accumulate in the batch reactor, whereas they may be washed away in columns.

Various types of water may be used to run treatability tests:

- Deionized water spiked with the targeted contaminant(s)
- Clean groundwater from the site spiked with the desired concentration of chlorinated solvents
- Contaminated groundwater from the site.

Some researchers use clean water in treatability tests; screening of new reactive media may be conducted with clean deionized water, whereas other treatability tests may be conducted with clean groundwater from the site. The clean water is spiked with known concentrations of the contaminants. In this way, researchers can better control or change feed concentrations (Sivavec, 1996). It is also easier to collect and ship clean groundwater from the site than it is to collect and ship groundwater already contaminated with volatile organics. It is important to run at least some tests with groundwater from the site (clean or contaminated) because of the important role played by native inorganic parameters in the site groundwater.

## 5.1 BATCH TESTING

Batch experiments generally are conducted by placing the media and contaminant-spiked water in septum-capped vials with no headspace. When samples are drawn from the vial for analysis, the vial is either sacrificed or nitrogen is added to fill up the headspace created (Sivavec, 1996). Nitrogen can be introduced into the vial by sampling with the dual-syringe technique. As the sample is drawn into one syringe, the other syringe (filled with nitrogen) slowly releases nitrogen into the headspace. Alternatively, deionized water may be used to replace the liquid withdrawn for analysis. In this way, organics concentrations can be measured as a function of time over multiple sampling events. The formation of reaction byproducts (hydrocarbon gases) in the vial can also be measured to differentiate any loss of reactants due to sorption rather than reaction.

Batch tests are useful screening tools because they can be run quickly and inexpensively. However, care should be taken in extrapolating the results to dynamic flow conditions. For example, O'Hannesin (1993) found that the column half-lives for TCE and PCE exceeded batch values by factors of 3 and 2, respectively, even though a higher iron-to-solution ratio was used in the columns than in the batch tests.

## 5.2 COLUMN TESTING

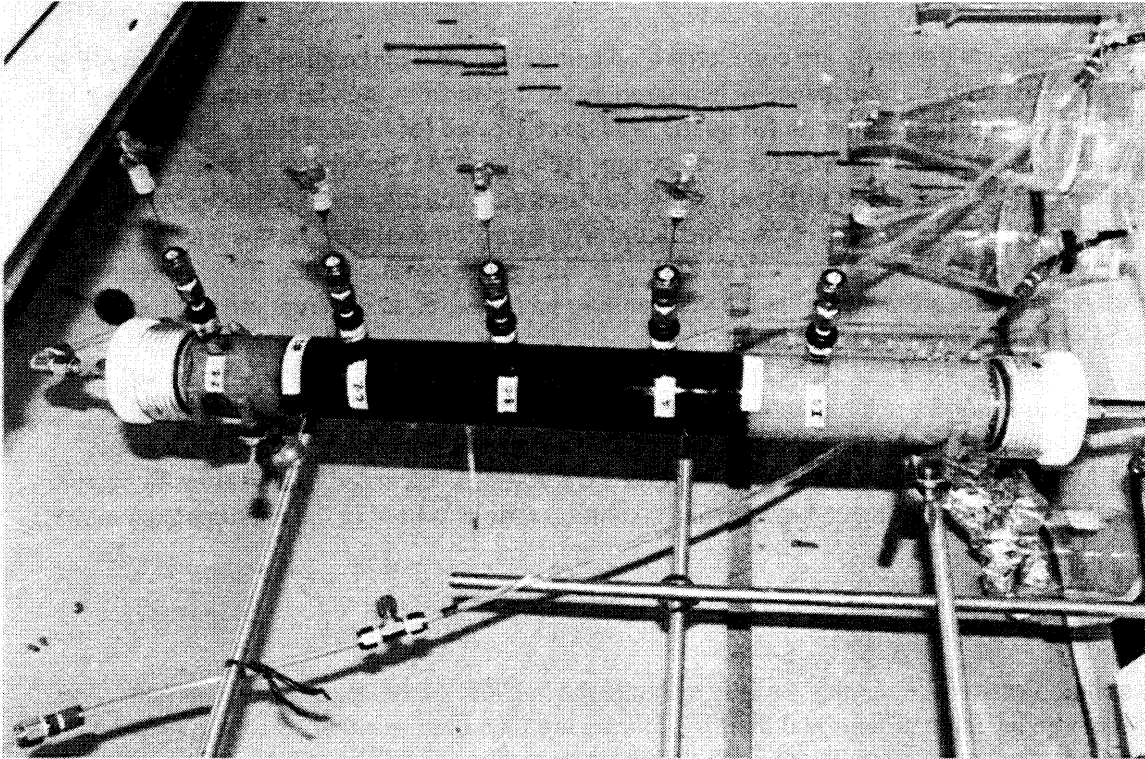
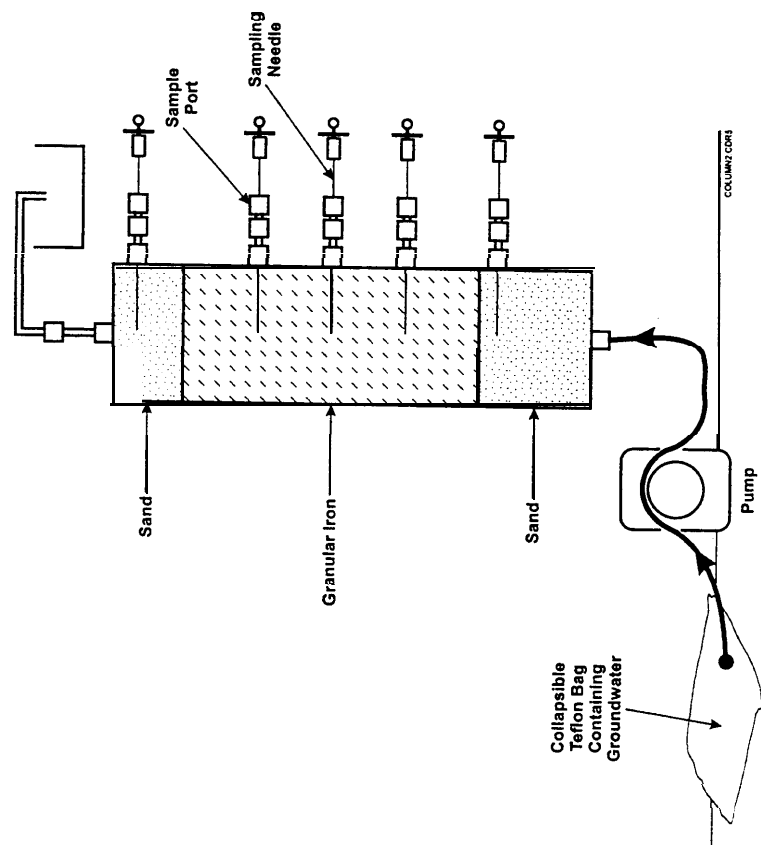
The main objective of column tests is to estimate the half-life of the degradation reaction. The half-lives of the organic contaminants and their byproducts are then used to either select the reactive medium or to design an appropriate flowthrough thickness for the reactive cell.

### 5.2.1 Design and Implementation of Column Tests

The design of a typical column setup is shown in Figure 5-1. A single column with multiple sampling ports along its length is used. The column is made from glass or Plexiglass<sup>TM</sup>. Strictly speaking, glass should be expected to have the least adsorptive or reactive effect with chlorinated organic compounds; however, no significant loss of organics has been found using Plexiglass<sup>TM</sup> columns (ETI, 1996). All fittings are stainless steel. Tubing is either stainless steel or Teflon<sup>TM</sup>. A small section of tubing through the peristaltic pump is made of Viton<sup>TM</sup> for added flexibility.

The column is packed with the reactive medium in such a way as to ensure a homogeneous matrix. One way of doing this is to make small aliquots of well-mixed media (e.g., iron and sand) and fill the column in small batches with each aliquot. Optionally, a section of sand may be placed above and below the reactive medium in the column to ensure good flow distribution. Average bulk densities, porosity, and pore volume, can be measured by weight (ETI, 1996).

The feed water is placed in a collapsible Teflon<sup>TM</sup> bag to prevent headspace as the bag empties out. The bag is filled by gravity flow to avoid aeration of the water. Water is circulated in the column from bottom to top to better simulate the flowrates likely to be encountered in the field. Sampling ports are equipped with gastight and watertight fittings. A nylon swage lock fitting may be used or a septum may be crimped onto the sample port. It is best to leave the sampling syringe needles permanently inserted into the column, with the tip at the center of the column. Valves with luer lock adapters are attached to the protruding ends of the needles outside the column (Sivavec, 1996; ETI, 1996). A luer lock plug is used to seal the needle between samples. Figure 5-2 shows a typical column test in progress.



Sampling should begin only after the concentration distribution in the column has reached steady state; that is, the net contaminant mass entering the column should be equal to the mass degraded in the column. Several pore volumes of contaminated water are generally required to be run through the column before it reaches steady state (Burris et al., 1995). Burris et al. (1995) also showed that the time (pore volumes) required to reach steady state varies with contaminant type. For example, water contaminated with PCE requires a longer time to reach steady state than does water contaminated with TCE.

Whenever a sample is to be drawn, a syringe is attached to the luer lock adapter on the needle and the sample is collected after a small amount of water is purged from the needle. The sample is drawn very slowly to create minimum disturbance in the flow. Most researchers conduct column experiments at room temperature. It is important to note, however, that temperature may be an important factor influencing reaction rate.

The flowrate through the columns should be set to simulate site conditions. Therefore, it is desirable to have good groundwater velocity data from the site at the location of the proposed barrier. We also need to take into account the fact that local groundwater velocity through the permeable barrier may be considerably higher than in the surrounding aquifer, especially in a funnel-and-gate system. Section 6.1 describes how expected groundwater velocity through the reactive cell can be determined through particle tracking maps. Actual flowrates through the column can be measured by collecting a timed volume of effluent. The experiment could be repeated over a range of flowrates to account for seasonal variations and other uncertainties. However, flowrate may not be a critical parameter for column testing. Gillham and O'Hannesin (1992) found that degradation rates were insensitive to flowrates in the range tested (59 to 242 cm/day). Once degradation rates have been determined through column tests, designing the flowthrough thickness of the reactive cell does require an accurate estimate of groundwater velocity.

*Concentration profiles* may be generated periodically for the chlorinated organics distribution in the column by collecting and analyzing samples from the influent, the effluent, and the intermediate sample ports after every 5 to 10 pore volumes. Eh and pH profiles of the column may be generated less frequently because of the higher sample volumes required for taking these measurements with typical probes. The column influent and effluent should be analyzed also for inorganics, such as major cations (Ca, Mg, Na, Fe, Mn, and K), major anions (Cl, SO<sub>4</sub>, NO<sub>3</sub>, and NO<sub>2</sub>), and alkalinity (bicarbonate).

Analysis of water samples collected from the column is done by the same general methods used for analyzing groundwater samples during site characterization (see Sections 3.2 and 3.3). Concentrations of chlorinated VOCs can be measured using a gas chromatograph-flame ionization detector (GC-FID) with purge and trap equipment. Water samples typically are drawn through sampling needles into a gastight syringe and are injected directly into the purge and trap through luer-lock adapters. Although chlorinated compounds can be detected using an electron capture detector (ECD), the GC-FID is suitable for general-purpose work because it can detect both a broad range of low-molecular-weight chlorinated compounds (e.g., TCE, DCE, and vinyl chloride [VC]), as well as nonchlorinated hydrocarbon byproducts such as ethene or ethane. Normally, the instrument is calibrated to detect compounds at the lowest concentrations feasible. **A typical detection limit for chlorinated hydrocarbons is 2 µg/L, provided that there is no strong matrix interference that requires dilution of the primary sample.**

Anions are typically measured using ion chromatography (IC) and cations by inductively coupled plasma (ICP). Detection limits for inorganic constituents also can depend on the matrix. There should be very little problem with analyte interference when deionized or low TDS water (synthetic or actual groundwater) is used; however, this may not be the case when high TDS water is used.

Redox potential (Eh) and pH are measured using appropriate probes (usually combination electrodes) in water samples immediately after they are withdrawn from the column. Accurate pH measurements can be taken only when the water is buffered or contains adequate concentrations of strong acid or strong base. Because most waters are near neutral to slightly alkaline and metallic compounds may raise the pH above 9, the pH range of 6 to 8 maybe the most difficult to obtain accurate readings. This is particularly true when the water in the column contains no buffer, such as carbonate.

Similarly, accurate Eh readings taken with a platinum electrode cannot be obtained unless the system is buffered with respect to electron transfer reactions; such a system is referred to as being “poised.” When a system is not well poised, Eh measurements do not reflect the abundance of electrons due to the combinations of half-cell couples. This can happen when the species present are not electroactive, i.e., they do not react rapidly on the electrode surface. Examples of nonelectroactive species are sulfate ( $\text{SO}_4^{2-}$ ), bicarbonate ( $\text{HCO}_3^-$ ), methane ( $\text{CH}_4$ ), and  $\text{N}_2$ . Complementary redox species that are electroactive include bisulfide ( $\text{HS}^-$ ) and ammonium ( $\text{NH}_4^+$ ). The problem of an unpoised system may exist only in water samples collected outside the reactive media. Within the reactive media the system should be well poised, for example, due to the  $\text{Fe}^0/\text{Fe(II)}$  redox couple and combinations of others couples. When the accuracy of Eh measurements is in question (because the system is poorly poised), Eh maybe calculated using ion concentrations. Some of the geochemical equations mentioned in Appendix C-1 permit the user to calculate Eh based on  $\text{HS}^-/\text{SO}_4^{2-}$ ,  $\text{N}_2/\text{NH}_3^+$ ,  $\text{CH}_4/\text{HCO}_3^-$ , or other redox couples.

Dissolved oxygen is difficult to measure offline, and may require an on-line flowthrough probe that excludes atmospheric oxygen from the sample. The dissolved oxygen concentration normally will be negligible when redox potential is negative, as should be the case when highly reducing metals such as iron or zinc are in equilibrium with the water. Therefore, dissolved oxygen measurements could be omitted during column tests, particularly if Eh can be measured with confidence.

### 5.2.2 Interpreting Column Data

For each water flow velocity and each column profile, chlorinated VOC concentrations are plotted initially as a function of distance through the reactive column (ETI, 1996). When the flowrate and porosity are known, distances through the column can be converted easily to residence times. A graph of VOC concentrations ( $\mu\text{g/L}$ ) versus residence time (in hours) can then be generated (see an example plot in Figure 5-3). A degradation rate constant,  $k$ , is calculated for each concentration profile using first-order kinetics.

$$C = C_0 e^{-kt} \quad \text{Eqn. 5-1}$$

When  $(C/C_0)$  is plotted against time in hours (see an example plot in Figure 5-4), the slope of the fitted line is the reaction rate,  $k$  ( $\text{hr}^{-1}$ ). The degree of fit can be determined by calculating the correlation coefficient ( $r^2$ ). The  $r^2$  value indicates how well the pseudo first-order model fits the experimental data. Once the rate constant is known, a half-life ( $t_{1/2}$ ) can be estimated for each organic contaminant of interest (TCE, PCE, etc.) in the influent. A half-life is the time period required to reduce the concentration of a contaminant by half. Table 1-1 in Section 1 shows the estimated half-lives for various chlorinated VOCs.

$$t_{1/2} = \frac{\ln(2)}{k} = \frac{0.693}{k} \quad \text{Eqn. 5-2}$$

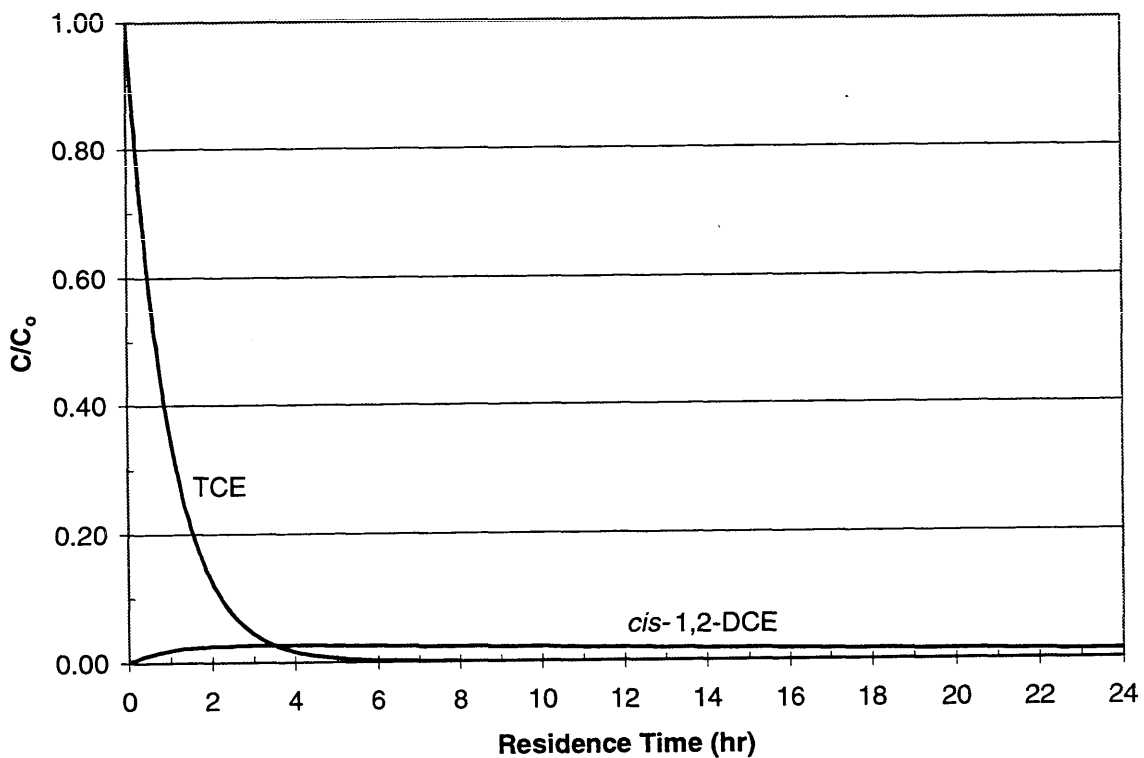


Figure 5-3. Column Concentration Profile of TCE and One of Its Byproducts, *cis*-DCE

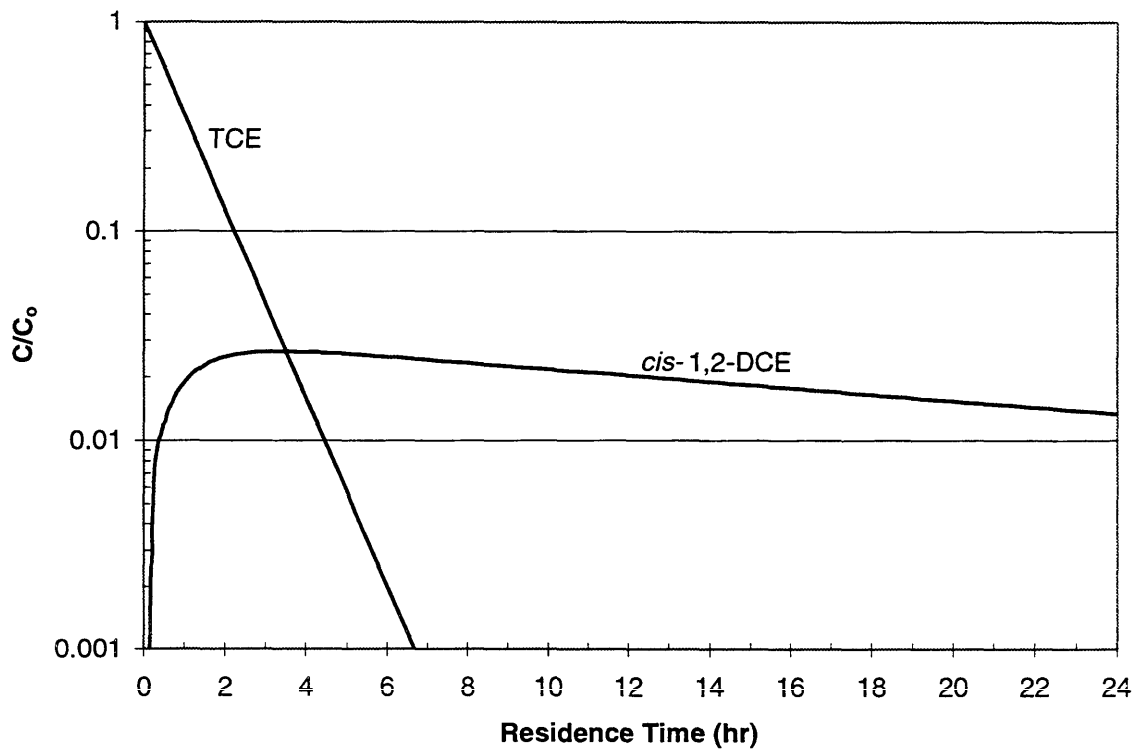


Figure 5-4. Pseudo First-Order Degradation Rate of TCE

When comparing the half-lives obtained for the same compound in columns with different reactive media, the reactive medium which provides the shortest half-life generally is selected. Costs, availability, buffering effects, and other factors also may be considered, as described in Section 4.

The required *residence time* for the permeable barrier design can be determined in several ways. Residence time can be estimated simply by the number of half-lives required to bring the concentration of the chlorinated VOC down to its MCL. For example, if TCE enters the reactive cell at 1,000 µg/L, eight half-lives are required to degrade TCE to an MCL of 5 µg/L. If the half-life of TCE from the column test was determined to be 2 hours, the required residence time in the reactive cell would be at least 16 hours. If there is more than one VOC of interest in the influent, the residence time is determined from the VOC with the longest half-life.

Alternatively, a residence time,  $t_w$ , can be estimated by rearranging equation 5-1, as:

$$t_w = (1/k) \ln (C_0/C) \quad \text{Eqn. 5-3}$$

However, this type of estimation does not take into account the residence times required to degrade byproducts (DCE, VC) that may be produced in the reactive cell. It may be that these byproducts are being produced and degraded concurrently, making it difficult to determine the reaction rates for the byproducts. The following procedure for determining residence time may provide a better estimate (ETI, 1996). The concentrations of all the chlorinated VOCs (influent and byproducts) are plotted against residence time in the column on the same graph. Figure 5-5 is an example of such a graph. The required residence time is the longest time required to bring all the contaminants down to their MCLs. In the example (Figure 5-5), the residence time is driven by the time required to bring VC down to its MCL. This type of estimation may require testing in longer columns or multiple columns in series if the simulated groundwater velocity is high.

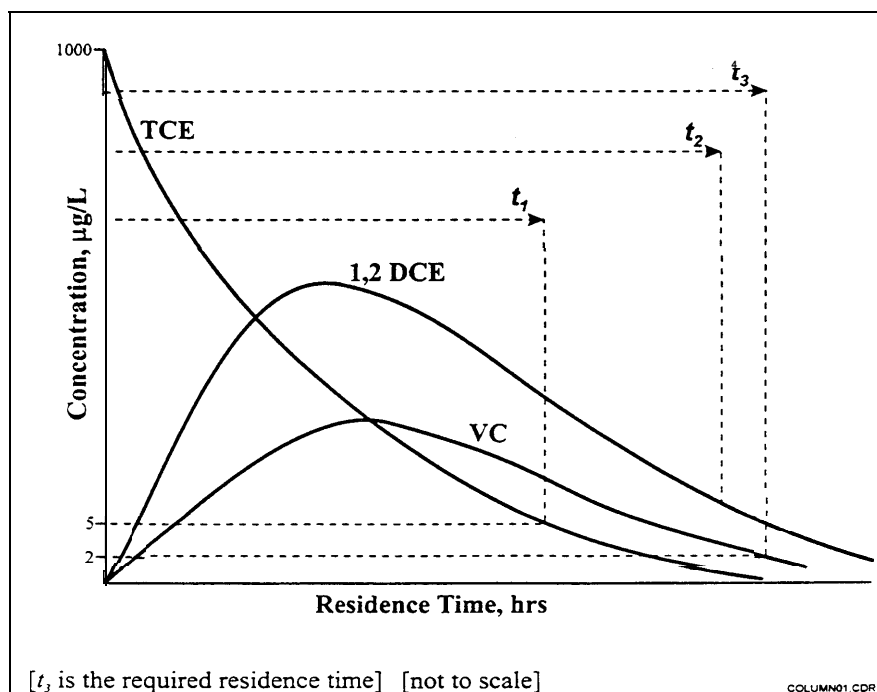


Figure 5-5. Example of a Column Profile of VOC Concentrations (Source: ETI, 1996)

The parameters pH and Eh can also be plotted against residence time (distance through column). Typically, as conditions become more anaerobic in the column, Eh should decline and pH should increase with increasing distance. Changes in anions, cations, and alkalinity between influent and effluent are also examined to understand the geochemical behavior of the system. Loss of dissolved calcium or magnesium could indicate the potential for precipitate formation in the reactive cell. Increase in dissolved iron in the effluent could indicate losses of ferrous iron from the cell. A geochemical evaluation of the inorganic chemistry data from column tests can provide a good basis for reactive media selection and longevity assessment (see Section 6.2).

### 5.2.3 Safety Factors

Some safety factors are required to adjust the degradation rate from laboratory data for field application. One important adjustment is the temperature. The temperature of the groundwater in the field application (typically 10 to 15°C) is generally lower than the room temperature of the experiment (typically 20 to 25°C). The empirical residence time may need to be increased to account for the lower temperature. For example, Senzaki and Kumagai (1988a and b) found that the half-life of 1,1,2,2-tetrachloroethane increased by 10 percent when temperature declined from 20 to 10°C. Jeffers et al. (1989) provide a discussion on the use of Arrhenius temperature dependence to adjust for the effects of temperature on degradation rate of organic compounds. The Arrhenius equation relates the reaction rate (k) to absolute temperature (T) as follows:

$$k \propto e^{-E/RT} \quad \text{Eqn. 5-4}$$

where E is the activation energy, and R is the universal gas constant (8.314 Joules/mol kelvin). Equation 5-4 can be rearranged as:

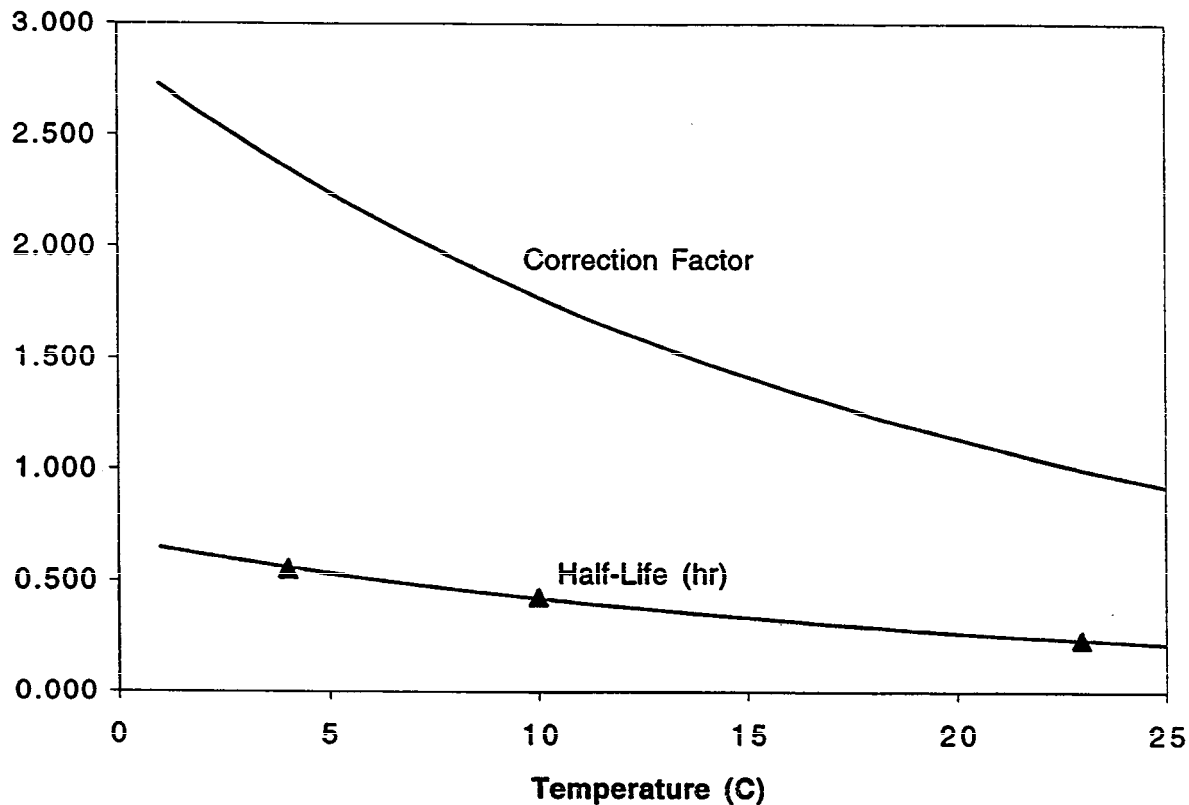
$$\ln k = (\ln A) - (E/RT) \quad \text{Eqn. 5-5}$$

where k = first-order reaction rate constant  
 A = frequency factor for the reaction  
 E = activation energy  
 R = ideal gas constant  
 T = absolute temperature

A plot of  $\ln k$  versus  $1/T$  should give a straight line with a slope of  $-E/R$  and an intercept on the  $1/T$  axis of  $\ln [(A)/(E/R)]$ . Experimental data from controlled-temperature column tests (ETI, 1997) resulted in the linear plot of TCE degradation rate constant versus temperature in Figure 5-6. The plot indicates that, at 15 °C in the field, TCE degradation rates could be expected to decline by a factor of 1.4 from those measured in the laboratory at 23 °C. Field observations at a test site in New Jersey have shown that the degradation rate declines by a factor of 2 to 2.5 at temperatures of 8 to 10 °C compared with laboratory rates. Similar results have been observed at other field sites.

Temperature versus reaction rate relationships have not as yet been determined experimentally for PCE. Given PCE's similar behavior to TCE in dehalogenation reactions, it may be assumed that a similar temperature factor would apply. During the design phase at existing sites, no temperature factors were applied to DCE or VC degradation rates, as measured rates of DCE and VC degradation in controlled-temperature experiments to date have shown little influence of temperature (ETI, 1997).





**Figure 5-6. Correlation of TCE Degradation Rates with Temperature (Source: ETI, 1997)**

The bulk density of the reactive cell in the field is generally lower than the bulk density measured in the laboratory because of different settling conditions for the medium (ETI, 1996). Therefore, the surface area of reactive medium per unit volume of groundwater in the field may be lower than that in columns. Degradation rates (or half-lives) are proportional to the specific surface area of the reactive medium (Gillham, 1996; Sivavec and Horney, 1995). The field residence time must be increased to account for the lower expected reactive surface area to volume of solution ratio. Currently, there is no clear indication of how large the bulk density correction factor should be. To some extent, this factor would depend on the efficiency of the emplacement and how well the reactive medium consolidates after emplacement. Gillham et al. (1993) reported that an increase in the surface area of iron by a factor of 5 caused the half-life for TCE to decline by a factor of about 2.5. Reduced iron surface area per unit volume of groundwater is the reason why 100 percent iron degrades faster than iron-sand mixtures. Also, finer iron granules generally have larger surface areas and faster degradation rates.

#### **5.2.4 Determining Flowthrough Thickness of the Reactive Cell**

Based on the groundwater velocity expected in the field reactive cell and the required residence time, the flowthrough thickness (b) of the field reactive cell can now be determined as:

$$b = V_x \cdot t_w \quad \text{Eqn. 5-6}$$

It should be noted that the groundwater velocity through the reactive cell is usually higher than the groundwater velocity in the aquifer because the conductivity of the reactive cell is usually higher than that of the aquifer. Hydrogeologic modeling (Section 6.1) is used to determine the expected groundwater velocity through the reactive cell. Additional safety factors may be incorporated into the calculated thickness to account for seasonal variations in the flow, potential loss of reactivity of the iron over time, and any other field uncertainties. Section 6.1 includes a discussion on hydrogeologic and geochemical factors affecting flowthrough thickness.

### **5.3 ACCELERATED AND LONG-TERM COLUMN TESTING**

Recently, some researchers have tried to use accelerated column tests to estimate the longevity of the permeable barrier (Sivavec, 1996). Their main approach has been to use accelerated aging techniques. Initially, degradation rates are measured in a column at the expected local velocity in the reactive cell. The flow is then increased to “age” the iron by passing a large number of flow volumes. Periods of low and high flow are alternated. At each low flow step, as soon as steady state is reached, measurements are conducted to estimate reaction rates, porosity losses (measured through tracer tests), inorganic profiles, and reaction products.

Caution should be exercised in interpreting the results of accelerated column tests. Equating 100 pore volumes at 20 feet/day in the laboratory with 1,000 pore volumes at 2 feet/day in the field may not provide an exact estimate, because the lower residence time in the accelerated column test may underestimate the amount of precipitation. Therefore, extrapolation to the field may not be easy. The advantage, on the other hand, is that a large number of pore volumes can be passed through the reactive medium in a short time. An alternative to the low-flow/high-flow approach is to run the columns at field groundwater velocities for very long times, i.e., for several months or years. An important objective in all such long-term tests is to study whether the inorganic profile ever levels off (Sivavec, 1996). Another objective is to ensure that the selected reactive medium can sustain its reactivity over longer periods of time (over several pore volumes). There is an indication that some reactive media (e.g., Fe-Ni bimetallic) may provide high reaction rates initially, but these rates may decline over long periods of time (Sivavec et al., 1997).

To extrapolate from column tests to field lifetime, the number of pore volumes is used as a scaling factor. For example, to translate from pore volumes to years, researchers may assume a velocity of 1 foot/day and a 4-foot wall thickness. With these conditions, 182 pore volumes would be equivalent to a lifetime of 2 years. Researchers suggest following the lifetime of each section of the column separately, because fouling is more likely to occur near the influent end where oxygen enhances precipitation (Sivavec, 1996).

### **5.4 ESTIMATING THE PERMEABILITY OF THE SELECTED REACTIVE MEDIUM**

Hydraulic conductivity (K) of the reactive medium is required to determine the flow velocity and residence time of groundwater through the reactive cell. Ideally, the K value for unconsolidated media is determined from constant head permeameter tests (Fetter, 1994). These tests are most reliably conducted in laboratories with conventional permeameter facilities. However, it may also be possible to use the laboratory treatability test columns for estimation of K by setting up the columns as constant head permeameters.

Constant head permeameters consist of an inlet tube with water level (head) maintained at a height slightly above the outlet level of the column. The water is allowed to flow through the reactive medium in the column until steady-state flow is obtained and the volume of water flowing out over a period of time is measured. K is determined from a variation of Darcy's law:

$$K = \frac{V \cdot L}{A \cdot t \cdot h} \quad \text{Eqn. 5-7}$$

where V is the volume of water discharging in time t, L is the length of the reactive medium sample, A is a cross-sectional area of the sample, and h is the hydraulic head difference across the column. It is important to prepare a uniformly packed column, maintain a hydraulic gradient across the column similar to that expected in the field, and ensure the absence of air bubbles in the column.